ARKIV FÖR FYSIK Band 2 nr 33

Communicated 24 May 1950 by M. Siegbahn and E. Hulthén

Determination of excitation energies of atoms with photo-tubes and oscillograph

By Lennart Huldt

With 6 figures in the text

The analysis of an atomic or molecular spectrum consists in determining the wave-numbers of the lines and then arranging the exit and the end levels, whose differences are the wave-numbers, into an energy level diagram. Although this may be troublesome for complicated spectra, the spectra of most neutral atoms have, as is well known, already been analysed. To-day, in addition to high-ionized atomic spectra, only some of the most complicated atomic spectra, such as those of the rare earths, uranium, etc., remain.

The intensity of a line in an emission spectrum depends on the excitation conditions in the light source and on the height of the upper energy level above the ground level, i. e. the excitation energy of the line. Only if self-absorption is present does the position of the lower level have any effect. If the excitation conditions are altered, the intensity is also altered in a manner depending on the excitation energy. This fact can be used to determine the relative positions of different upper levels in a spectrum, and so facilitate the analysis of an unknown spectrum.

As a concrete example we shall imagine the following experiment. Suppose an atomic spectrum is being emitted from an alternating current discharge of, say 50 p/s. The intensity of any line in the spectrum then varies with a frequency of 100 p/s from a minimum value (which can be 0, if the discharge is interupted at every turn in the current) to a maximum. If the circumstances in the discharge are to be described by the absolute temperatur T, we can express the intensity of the line by means of the Boltzmann factor. If we measure the intensity of the line photo-electrically, the measuring instrument indicates the current intensity I, where

$$I = \alpha\, i\, e^{-E/kT}.$$

α is an apparatus constant, depending on the geometrical, optical and electrical arrangements, i is an »intensity factor» = the transition probability times the statistical weight; E is the excitation energy, and k is Boltzmann's constant. The difference between the photo-currents of two lines will then be:

$$I_2 - I_1 = \alpha_2\, i_2\, e^{-E_2/kT} - \alpha_1\, i_1\, e^{-E_1/kT}.$$

The apparatus coefficients α_1 and α_2 can be varied arbitrarily within wide limits, independently of each other, by means of optical or electrical manipulations. We shall write this difference:

$$I_2 - I_1 = \alpha_1 i_1 \left(\frac{\alpha_2 i_2}{\alpha_1 i_1} e^{\frac{E_1 - E_2}{kT}} - 1 \right) e^{-\frac{E_1}{kT}},$$

T varying periodically from T_{max} to T_{min} (which may be practically 0).

With a cathode-ray oscillograph the two currents can be studied as a function of time (Dieke et alt. 1946). This function will be periodical with a frequency of 100 p/s. If α_1 and α_2 are varied, the difference $I_2 - I_1$ will be either positive or negative, or alter its sign during a period. It is, however, not possible to get $I_2 - I_1 = 0$ during a full period, unless

$$E_1 = E_2,$$

i. e. the two lines have a common upper level, or the two upper levels have the same height above the ground level. In this case, by varying α_1 and α_2 so that $\alpha_2 i_2 / \alpha_1 i_1 = 1$, one can obtain:

$$I_2 = I_1$$

during the course of the whole period.

Instead of recording the difference between the two currents as a function of time, one can connect the two currents to either of the two plate couples of the oscillograph. I_2 is then obtained as a funtion of I_1. The properties of this curve is most simply demonstrated by the quotient:

$$\frac{I_2}{I_1} = \frac{\alpha_2 i_2}{\alpha_1 i_1} e^{\frac{E_1 - E_2}{kT}}$$

with T as a parameter.

It is obvious that the curve appearing on the screen bends towards the I_1- (x-)axis if $E_1 > E_2$, and in the opposite direction if $E_1 < E_2$. If $E_1 = E_2$, the quotient is constant,

$$\frac{I_2}{I_1} = \frac{\alpha_2 i_2}{\alpha_1 i_1},$$

during the whole period, and the curve is linear.

The magnitude of the curvature will thus be a measure of the magnitude of the positive or negative difference $E_1 - E_2$, and in any case the direction of the curvature will determine the sign of $E_1 - E_2$. In this way we have a means of determining the order of the upper levels, and thus of drawing up the energy level diagram from a spectrum.

In applying the method it is significant that I in the above equations may be replaced by $\frac{dI}{dt}$ or a higher derivative, which will only change the apparatus coefficients α. In many electrotechnical apparatus one does not measure the currents but their derivatives.

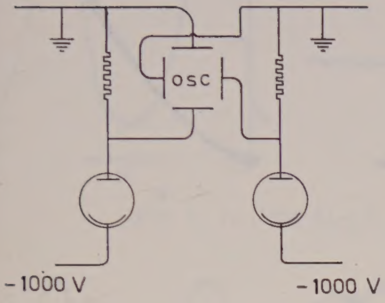

Fig. 1.

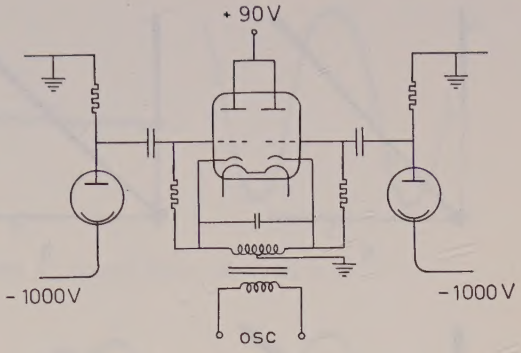

Fig. 2.

At this point some comments might well be made. First, it is naturally not necessary to use such a rapidly varying light source as an a. c. lamp, or to record the currents with an oscillograph. In principle it should be possible to use, for example, a d. c. glow discharge and to measure the currents with an ordinary galvanometer. The different data—the different points on the curve—will then be obtained by varying the voltage of the lamp. The measurements of the light intensities might even be performed photographically instead of photo-electrically. However, this would be very lengthy.

A serious fundamental objection may be raised against the assumption of thermodynamical equilibrium in an electrical discharge and, therefore, of the justification of the Boltzmann factor. If statistical equilibrium is not attained, as in most glow discharges, the excitation can often be determined by an approximately uniform »electron temperature». In other cases the formal quantity T, inserted in the Boltzmann factor, increases with E. This is also the case when a spectrum line, coming from several regions with different temperatures, is studied (LOCHTE-HOLTGREVEN and MAECKER, HULDT). The above methods still maintain their validity qualitatively, however, if T increases more slowly than E, as should always be the case. Then $\frac{E_2}{T_2} - \frac{E_1}{T_1}$ has the same sign as $\frac{E_2 - E_1}{T}$ given above.

To test the method on a simple and well-known spectrum, we chose the mercury atomic spectrum. An ordinary Hg a. c. lamp, fed from the main 50-periodic voltage, illuminated simultaneously the input slits of two glass monochromators (one a van Cittert double monochromator, manufactured by Kipp and Zonen, the other a Hilger constant deviation spectrometer, supplied with an output slit). At the output slit of each monochromator a commercial multiplier photo-tube (RCA 931) was mounted. The photo-currents were led to a cathode-ray oscillograph (du Mont 304) in each of the two ways described.

The circuits are shown in the Figs. 1 and 2. The high voltage in the tubes was derived from dry batteries as being certainly free from a. c. ripple. (The high voltage aggregate and the dynods are omitted in the diagrams.) The arrangement giving the I_1/I_2 curve is very simple (Fig. 1) and requires no amplifier but that of the oscillograph. When recording the difference $I_2 - I_1$ as a

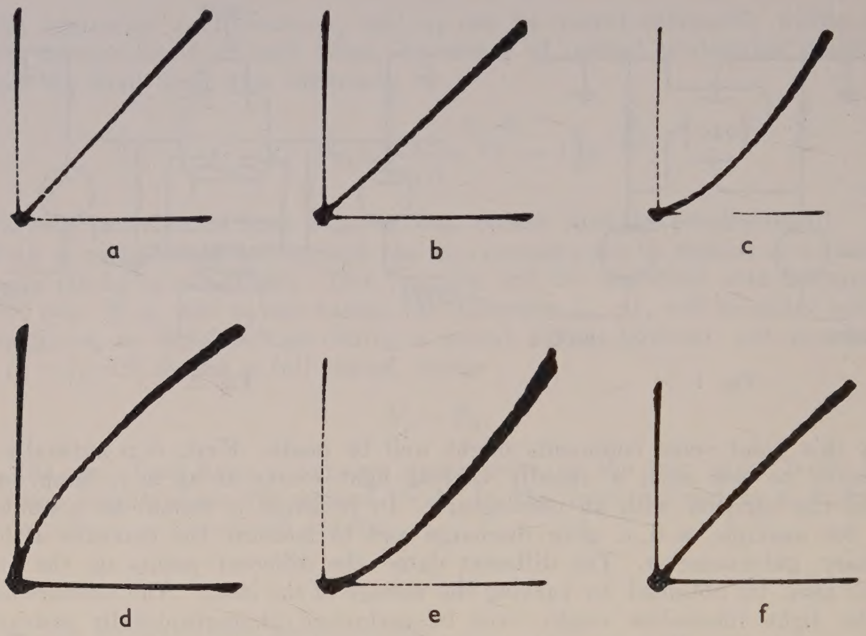

Fig. 3. I_1 (horizontal axis) against I_2 (vertical axis)

a) I_1 5461 Å; I_2 5461 Å. $E_1 - E_2 = 0$
b) I_1 5461 Å; I_2 4047 Å. $E_1 - E_2 = 0$
c) I_1 5461 Å; I_2 5791 Å. $E_1 - E_2 = -1.11$ e. v.
d) I_1 5791 Å; I_2 4358 Å. $E_1 - E_2 = 1.11$ e. v.
e) I_1 5461 Å; I_2 4077 Å. $E_1 - E_2 = -0.19$ e. v.
f) I_1 5791 Å; I_2 4077 Å. $E_1 - E_2 = 0.92$ e. v.

function of time, a double triode tube and a transformer were used (Fig. 2). In the available wave-length interval the following mercury lines are suitable for recording (arranged according to increasing excitation energy E):

5460.74 Å 4358.34 Å 4046.56 Å (E = 7.73 e. v.)
4077.83 Å (E = 7.92 e. v.)
5790.66/89.69 Å (not resolved) 5769.60 Å (E = 8.84 e. v.).

Different combinations of these lines were recorded on the oscillograph screen by both the methods described (I_2/I_1 method and $I_2 - I_1$/time method). Photographs of the I_2/I_1-curves are shown in Fig 3. The curves (a) and (b) are indentical in appearance, a straight line, (a) obtained with the same line feeding both the photo-tubes, (b) from two different lines with a common upper level. The curves (c)—(f), on the contrary, show an obvious curvature towards the axis corresponding to the higher excitation energy. Even Fig. 3 e corresponding to an energy difference of only 0.19 e. v., manifests an appreciable curvature. The curvature of Fig. 3 f with $E_1 - E_2 = 0.92$ e. v. is remarkably less. This anomaly might possible be explained by the above-mentioned increase in the electron temperature with E.

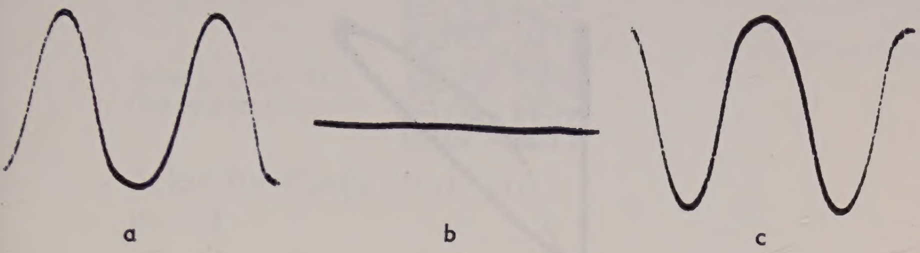

Fig. 4. I_2 (4358 Å) — I_1 (5461 Å) against time. $E_1 - E_2 = 0$.

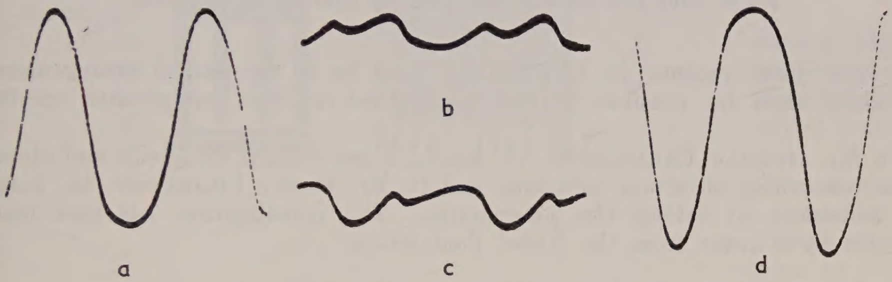

Fig. 5. I_2 (4358 Å) — I_1 (5791 Å) against time. $E_1 - E_2 = 1.11$ e. v.

Fig. 4 gives photographs of the $I_2 - I_1$/time curve, obtained with the lines 5460.74 Å (I_1) and 4358.34 Å (I_2), having the same excitation energy. Fig. 4 a shows I_2/time, 4 c shows I_1 (in the opposite direction) against time and 4 b the difference curve, the photo-currents regulated to give a horizontal straight line, i. e. $I_1 = I_2$. The regulation here was simply carried out by varying the slit widths. Fig. 5 shows the same for the lines 5461 Å (I_2) and 5791 Å (I_1) with different upper levels ($E_1 - E_2 = 1.11$ e. v.). From (a) towards (d) I_2 decreases ($I_2 = 0$ in d) and I_1 increases ($I_1 = 0$ in a), as the widths of the slits are varied, without the curve ever becoming a straight line.

From Figs. 3, 4 and 5 it seems evident that the I_2/I_1 method is the clearest and the most sensible one for determining the relative positions of the upper levels of two lines and for estimating the distance between them. On the other hand, the $I_2 - I_1$/time method permits amplifying the ordinate $I_2 - I_1$, which combined with some calibration method will possibly bring about sufficient sensibility. Further investigations will deal with this problem.

The diffuse appearance of the curves depends partly on the high frequency fluctuations in the photo-current (diminished by the condenser connected in parallel with the primary windings of the transformer). Further, the mercury arc lamp exhibtis a phase shift between its different parts. As two different images of the lamp were used in the experiments reported here, one on each collimator slit, a small phase shift between the photo-currents could not be avoided. Accordingly, each curve in Fig. 3 is a somewhat open coil (which cannot, however, be seen in the reproductions). If the lamp were displaced somewhat from its position, this coil became widely open, as is seen from Fig. 6. This phase shift also entailed some difficulties in getting a straight line in Fig. 4. Consequently,

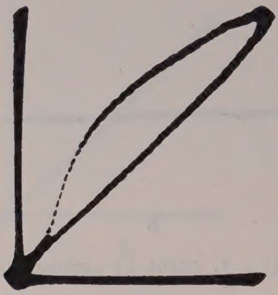

Fig 6. 5461 line on both axis with the light source displaced.

the first improvements in the method must be in the optical arrangements. It might then be possible to test the method on more complicated spectra.

To Mr. GUNNAR ERLANDSSON, fil. kand., I am obliged for advice and discussions concerning electronic problems and to Mr. BENGT LILJEKVIST, fil. kand., for assistance in taking the photographs. The investigation has been made possible by a grant from the Nobel Foundation.

Fysiska Institutet, Stockholms Högskola, May 1950.

REFERENCES: **G. H. Dieke** et alt., J. Opt. Soc. Am., 1946, *36*, 185. — **W. Lochte-Holtgreven** and **H. Maecker,** ZS f. Ph., 1937, *105*, 1. — **L. Huldt,** Ark. f. mat., astr. o. fys., 1948, *36 A*, Nr. 3; Dissert., 1948, Stockholm, pp. 22—23.

Tryckt den 22 september 1950.

Uppsala 1950. Almqvist & Wiksells Boktryckeri AB